# Special Report 85-22

November 1985

**US Army Corps
of Engineers**

Cold Regions Research &
Engineering Laboratory

# *Comparison of extraction techniques and solvents for explosive residues in soil*

Thomas F. Jenkins and Daniel C. Leggett

AD-A166 474

DTIC FILE COPY

DTIC
ELECTE
APR 7 1986
S B

86 4 7 068

| REPORT DOCUMENTATION PAGE | | READ INSTRUCTIONS BEFORE COMPLETING FORM |
|---|---|---|
| 1. REPORT NUMBER<br>AMX-TH-TE-TR-85041 | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER |
| 4. TITLE *(and Subtitle)*<br>COMPARISON OF EXTRACTION TECHNIQUES AND SOLVENTS FOR EXPLOSIVE RESIDUES IN SOIL | | 5. TYPE OF REPORT & PERIOD COVERED |
| | | 6. PERFORMING ORG. REPORT NUMBER<br>Special Report 85-22 |
| 7. AUTHOR(s)<br>Thomas F. Jenkins and Daniel C. Leggett | | 8. CONTRACT OR GRANT NUMBER(s)<br>Order no. A1-5-R0001-XX-A1-48 |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>U.S. Army Cold Regions Research and Engineering Laboratory<br>Hanover, New Hampshire 03755-1290 | | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS |
| 11. CONTROLLING OFFICE NAME AND ADDRESS<br>U.S. Army Toxic and Hazardous Materials Agency<br>Aberdeen Proving Ground, Maryland | | 12. REPORT DATE<br>November 1985 |
| | | 13. NUMBER OF PAGES<br>37 |
| 14. MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)* | | 15. SECURITY CLASS. *(of this report)*<br>Unclassified |
| | | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE |

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution is unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

| | |
|---|---|
| Chemical analysis | RDX |
| Explosives | Soil pollution |
| HMX | Soils |
| Pollution | TNT |
| | TNB |

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Extraction of TNT, TNB, RDX and HMX from two soils was studied in terms of process kinetics and recovery. Two solvents, acetonitrile and methanol, and four extraction techniques, Soxhlet, ultrasonic bath, mechanical shaker and homogenizer-sonicator were compared. The results were complex in that some interactions among analyte, method and solvent were found. Acetonitrile was found to be clearly superior to methanol for RDX and HMX. Soxhlet and ultrasonic bath generally recovered more than homogenizer or shaker, although a complicating factor is that all techniques were not necessarily at equilibrium. In terms of sample throughput, the ultrasonic bath and shaker are preferred over Soxhlet

DD `FORM 1473` `1 JAN 73` EDITION OF 1 NOV 65 IS OBSOLETE

20. Abstract (cont'd).

and homogenizer-sonicator. The ultrasonic bath generally approached equilibrium more rapidly than the shaker so it appears to be the best overall choice. Another complicating factor is that times to reach equilibrium were different for the two soils and for the different analytes. This points to the need for more kinetic studies on other soils and sediments.

## PREFACE

The contents of this report are not to be used for advertising or promotional purposes. Citation of brand names does not constitute an official endorsement or approval of the use of such commercial products.

| Accession For | |
|---|---|
| NTIS GRA&I | ✓ |
| DTIC TAB | ☐ |
| Unannounced | ☐ |
| Justification | |
| By | |
| Distribution/ | |
| Availability Codes | |
| Dist | Avail and/or Special |
| A-1 | |

CONTENTS

ILLUSTRATIONS

Figure

TABLES

Table

# COMPARISON OF EXTRACTION TECHNIQUES AND
# SOLVENTS FOR EXPLOSIVE RESIDUES IN SOILS

by

Thomas F. Jenkins and Daniel C. Leggett

## INTRODUCTION

The Army is interested in analyzing soils for explosive contaminants
both to aid in decontaminating facilities and to stop pollution. Army
laboratories or contractors hired to conduct surveys have not been supplied
with a uniform protocol for extracting these contaminants from soils. As a
result, various extraction techniques and solvents have been used, often
without sufficient validation of their use for particular contaminants in
particular soils. Thus the quantitative and in some cases the qualitative
accuracy of the results of soil contaminant surveys is variable and not
always known. The purpose of this work was to identify or develop a single
methodology for analyzing explosive contaminants in soils that was as
accurate and as rapid as possible.

Since reverse-phase HPLC (High Performance Liquid Chromatography)
would most likely be the analytical method of choice for mixtures of
explosive contaminants (Jenkins et al. 1984), we concentrated our efforts
on those solvents that are compatible with this analytical technique.
Desirable properties of such solvents are miscibility with water and low UV
absorption at 254 nm. These solvents include methanol and other alcohols,
acetonitrile and tetrahydrofuran. When GC (Gas Chromatography) or other
type of analytical finish is used, other solvents may be more appropriate.

Goerlitz and Law (1975) extracted TNT and RDX from soils with
acetone-hexane prior to GC analysis. The method involved a 12-hour equili-
bration period with acetone alone, followed by addition of hexane and two
additional extractions with no waiting period. Three extractions were
required for quantitative (93-99%) recovery because the first extraction
yielded only 55%. However, it is hard to tell how much of this was attri-
butable to incomplete solvent recovery and how much to incomplete extrac-
tion.

As part of a previous preliminary study in our laboratory, acetone, methanol, acetonitrile and tetrahydrofuran were compared for extracting TNT, TDX and HMX from a soil and a sediment (Cragin et al. 1985). A single batch extraction was used, as little additional recovery was obtained in a second extraction. The solvent-to-soil ratios were higher than those of Goerlitz and Law, however, and the solvent was not diluted with hexane prior to its separation from the soil. Samples were placed in an ultrasonic bath for 5 minutes followed by 1 hour of shaking. Extraction recovery varied with type of sample and the concentration of explosive present. Acetone interfered with quantification of HMX by HPLC. Recoveries from the other three solvents were within 20%.

Both Goerlitz and Law (1975) and Cragin et al. (1985) used unfortified, naturally contaminated soils and recoveries were based on the amounts obtained by exhaustive extractions. Miller et al. (1983) tested single batch extractions with acetone, acetonitrile and methylene chloride/methanol (95/5) on a sediment that was fortified with eight different explosive compounds. The best overall solvent was methylene chloride/methanol. Recoveries of TNT and RDX ranged from 87-107%, but tetryl was poorly recovered. It thus appears that any of several solvents or solvent mixtures could be used to extract explosive compounds. Since we are mainly interested in using reverse-phase HPLC analysis, we chose to evaluate methanol and acetonitrile since these solvents can be analyzed directly or after dilution with water. Acetone is good but causes some interference with early peaks. Tetrahydrofuran is also good and is compatible with HPLC, but appeared to offer no advantage over acetonitrile or methanol so was not evaluated further.

Unfortunately, the state of the art is not such that we can reliably match extraction solvents with particular contaminants to obtain the best solvent-contaminant pairing, and selections have been largely empirical in the past. In a review of the literature from 1960 to 1981, Dao et al. (1983) found methanol and acetone to be the most frequently used single solvents for soil pesticide analyses. Nonpolar solvents such as hexane are seldom used, presumably because they don't work as well, even for nonpolar residues. A reason for this apparent contradiction is given by Freeman and Cheung (1981), who suggest that failure to properly match the solubility parameter of the extracting solvent with that of the soil organic matter (the presumed site of sorption) will result in low recovery regardless of

equilibration time. This apparent contradiction of equilibrium thermo-
dynamics is explained as failure of the solvent to "swell" or "wet"
internal polymer surfaces, resulting in failure of the system to come to
equilibrium within the practical time constraints imposed by the need to
complete the analysis. On the other hand, we cannot ignore the solubility
of contaminants in the extracting solvent either, particularly when they
are present in concentrations that would exceed the ability of the solvent
to dissolve them. Thus, solubility in extracting solvents during
extraction and subsequent work-up will be considered carefully here.

In view of the foregoing discussion, careful attention will also be
paid to extraction kinetics, as the shortest practicable equilibration time
is desirable in a method. The usual ways of decreasing contact times are
shaking, homogenization and sonication. Drying of sediments and soils
prior to extraction was also considered in an earlier study (Cragin et al.
1985). This point deserves some comment here. It was found that TNT,
RDX and HMX were extracted as efficiently from wet soils as from freeze-
dried soils using methanol as the extracting solvent. It appears that this
is generally the case when polar solvents are used. Use of water-imiscible
solvents, however, generally leads to lower recoveries from wet sediments
regardless of the extraction technique used.

Haddock et al. (1983) extracted anthracene better from dry sediments
than from wet sediments 8 days after spiking, using either benzene or
benzene-acetonitrile (13:7). Peterson and Freeman (1982) showed that using
Soxhlet extraction for dried sediments gave higher recoveries of added
phthalate esters than those that they obtained from wet sediments using
methylene chloride as the extracting solvent. This same study also indi-
cated that ultrasonication with this solvent gave recoveries that were as
high as or higher than did Soxhlet (presumably when both were done on dried
sediment) and required only 1 hour for completion as opposed to 48 hours
for Soxhlet. This latter finding is similar to that of Wegman and Hofster
(1982), who studied extraction of a group of organochlorine pesticides
added to sediment for varying lengths of time. They found that shaking,
either with petroleum ether or with 1:1 acetone-petroleum ether, gave
recoveries as high as those that they obtained from Soxhlet extraction
using these solvents. They also found that acetone-petroleum ether was
superior to petroleum ether and that it extracted as efficiently from wet
as from dry sediment. Acetone, however, appeared to be better than the

3

mixed solvent for extracting contaminants from wet sediment. These conclusions are not supported by rigorous statistical evaluation.

These studies are mentioned because they suggest that extended Soxhlet extraction may not necessarily give the highest recovery, contrary to popular expectation. One reason for this could be irregular contact with the sample caused by channeling or the nonuniform nature of the sample itself. These types of problems would naturally tend to be reduced by vigorous shaking, homogenizing or sonicating. On the other hand, Sporstol et al. (1983) claim that Soxhlet extraction is generally superior to ultrasonication for natural contaminants present in sediments. However, their study suffers from a serious flaw in that Soxhlet extraction of dried sediment is compared to ultrasonic extraction of wet sediment using dichloromethane as extractant. As pointed out above, this is not a fair comparison, and extraction techniques should be evaluated using similar sample preparation. The addition of 5% methanol to the extractant significantly improved recoveries from the wet-ultrasonicated sediment, another indication that moisture might have been the reason for low recovery.

In addition to their being the best choice of solvents for analysis by reverse-phase HPLC, methanol and acetonitrile are completely miscible with water so that they can be used for extracting either wet or dried samples. For this study, dried samples will be used since it was shown that freeze-drying or air-drying produce small or insignificant losses of TNT, RDX and HMX (Cragin et al. 1985). The small losses are compensated for by the ease of working with dry material, which can be sampled more precisely. Finally, we chose to work with "naturally contaminated" sediments rather than with spiked sediment because of the additional ambiguity that the latter introduces (Peterson and Freeman 1982, Sporstol et al. 1983, Haddock et al. 1983, Cragin et al. 1985).

The objective of this study was to determine which of several alternative extraction procedures gave the best recoveries of HMX, RDX and TNT for contaminated soils. Methanol and acetonitrile were examined as extraction solvents because preliminary tests indicated good results for explosive residues and because they are suitable for use with the existing HPLC analytical procedure. The extraction methods evaluated were: continuous Soxhlet extraction, batch extraction by equilibration with solvent on a wrist-action shaker, batch extraction using a soil-plant homogenizer and batch extraction by equilibration with solvent in a bath sonifier.

## EXPERIMENTAL

### Analytical instrumentation

All analytical determinations for HMX, RDX, TNB, TNT and DNT were
obtained using reverse-phase HPLC (Jenkins et al. 1984). The instrumental
setup utilized a Perkin Elmer Series 3 pump with a Rheodyne 7125 loop in-
jector and a Spectra-Physics SP8300 fixed 254-nm UV detector. Peak areas
were quantified using an HP 3390A Integrator. Analyses were obtained on a
Supelco 25 cm x 4.6 mm LC-8 column (5μm) using a mobile phase of methanol/
acetonitrile/water, 38:12:50 (v/v/v). Samples were injected by over-fil-
ling either a 20-μL or a 100-μL sample loop. Analyses were obtained in
duplicate and mean values reported.

### Chemicals

All analytical standards for HMX, RDX, TNB, TNT and DNT were prepared
from Standard Analytical Reference Materials (SARMs) obtained from the
U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground,
Maryland. Samples were dried to constant weight in a vacuum desiccator
over dry calcium chloride in the dark.

The methanol and acetonitrile used to prepare the mobile phase for
HPLC determinations and as extraction solvents were either Baker HPLC grade
or Mallinckrodt Chrom AR HPLC grade solvents. Water used in the prepara-
tion of the HPLC mobile phase and as sample diluent was purified using a
Milli-Q Type I Reagent Grade Water System (Millipore Corporation). Methan-
ol, acetonitrile and water were combined in the proper proportions and
vacuum-filtered through Whatman GF-F glass microfibre filters to remove
particulate matter and degas the solvent.

### Soils

The soil samples used for extraction experiments were collected at the
Iowa Army Ammunition Plant (AAP) on 25 and 26 July 1983. Soil no. 6 was
obtained from an old ordnance-burning area that had not been used since
1981. Soil no. 2 was obtained from the surface of an old disposal lagoon.
Each soil was air-dried to constant weight, ground with a mortar and
pestle, and passed through a no. 30 mesh sieve. Both soils were placed in
individual Nalgene bottles and mixed thoroughly on a roller mill to obtain
as homogeneous a sample as possible to allow comparison of various extrac-
tion techniques.

## Kinetic studies

Kinetic studies were conducted on four different procedures for two different soils. These were solvent extraction methods using a wrist-action shaker, a bath sonifier, a soil-plant homogenizer and a Soxhlet extractor. In each case methanol and acetonitrile solutions containing a DNT internal standard were individually tested at a soil-to-solvent ratio of 1 g/25 mL. Tests indicated that DNT did not sorb to soil at measurable levels in the presence of the extracting solvent.

### Soil-plant homogenizer

For soil no. 6, two 1-g samples of soil were placed in 45-mL Pyrex centrifuge tubes; 25 mL of a methanol solution containing a DNT internal standard was added to one and 25 mL of an acetonitrile solution containing a DNT internal standard was added to the other. Each sample was ground in a soil-plant homogenizer (PT 10/35 Brinkmann Homogenizer with PTA 20S Generator) at a setting of 4 for periods of 1, 2, 4, 8 and 16 minutes (Fig. 1). After each period, the sample was centrifuged at 3500 rpm until the solution cleared (5-15 min), a 2-mL portion of clear supernatant was
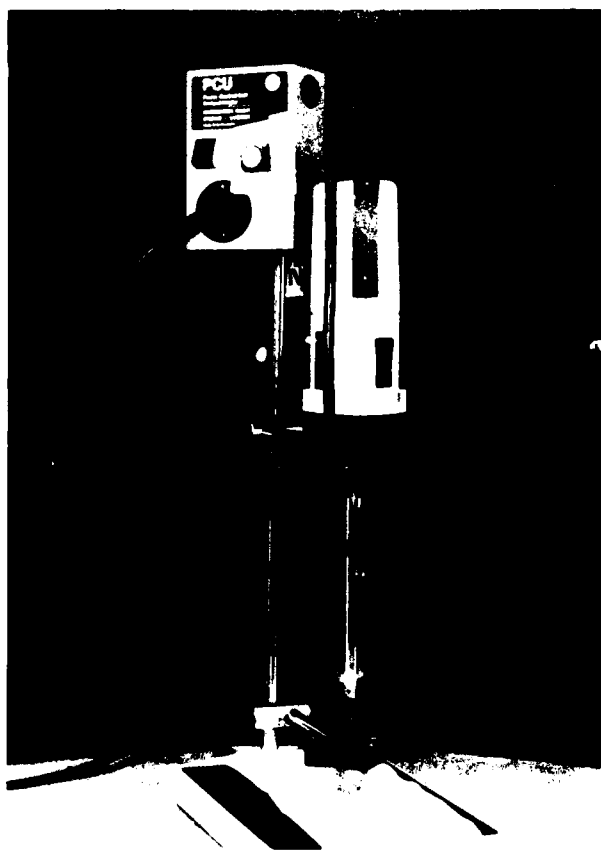


Figure 1. Brinkmann soil-plant homogenizer.

6

removed and the tube was replaced on the homogenizer. Each 2-mL aliquot was mixed with 2 mL of water and filtered through a 0.45-μm Gelman Acrodisc CR disposable filter assembly using a 10-cm$^3$ B-D disposable syringe. The first 1-mL portion of the filtrate was discarded and the remainder saved for HPLC analysis. There was significant solvent evaporation during homogenizing and centrifuging, but use of the internal standard corrected for this factor. Soil no. 2 was treated in an identical manner, except grinding times were 5, 10, 20 and 60 minutes.

### Bath sonifier

For this procedure, 2-g samples of soil no. 6 were placed in two 2.5-cm x 20-cm screw cap test tubes equipped with a Teflon-lined cap. We added 50 mL of either methanol or acetonitrile containing a DNT internal standard. The soil in each tube was dispersed with a vortex mixer (Vanlab Model K-550-G) for 1 minute and placed in a sonic bath (Cole-Parmer Model 8845-60) for periods of 1, 2, 4, 8, 16, 32, 64 and 240 mintues (Fig. 2). The samples were redispersed with the vortex mixer between periods. After each period, the tubes were centrifuged at 3500 rpm for 5 minutes, and a 5-mL portion of the supernatant was removed with a volumetric pipette, mixed with 5 mL of water and filtered as described above. Soil no. 2 was treated as described above, except equilibration times studied were 15, 30, 60, 120, and 420 minutes.
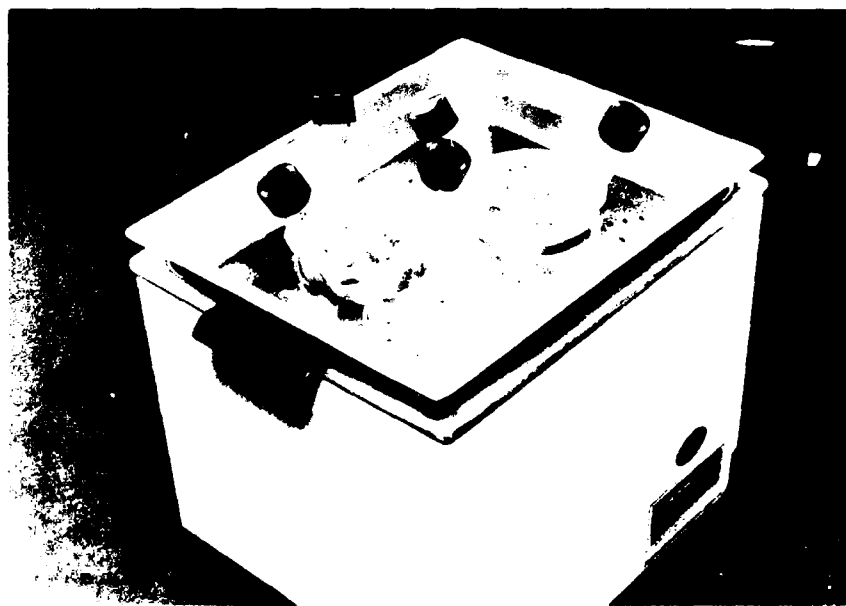


Figure 2. Vanlab model K-550 bath sonifier.

7
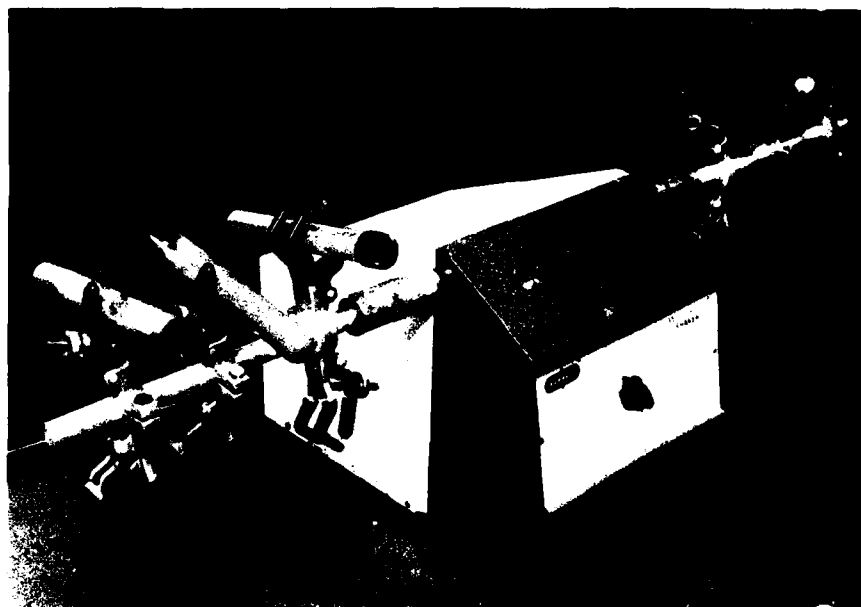
Figure 3. Burrell model 75 wrist-action shaker.

### Wrist-action shaker

Two 2-g samples of soil no. 6 were placed in 2.5-cm x 20-cm screw cap test tubes and 50 mL of either methanol or acetonitrile containing a DNT internal standard was added. The soil was dispersed with a vortex mixer for 1 minute and placed on a wrist-action shaker (Burrell Model 75) at maximum speed for periods of 10, 30, 60, 90, 150, 240, 480 and 1440 minutes (Fig. 3). After each period, 5-mL samples were removed and processed as described for the bath sonifier experiment and the soil redispersed with the vortex mixer prior to beginning the next time interval. Soil no. 2 was treated in a similar fashion, except samples were taken for analysis at 30, 60, 120, 240, 1440 and 2880 minutes.

### Soxhlet extractor

Two 16-g samples of soil no. 6 were placed in Soxhlet extraction thimbles (Whatman, cellulose) and extracted on Soxhlet extractors with 400 mL of either methanol or acetonitrile containing a DNT internal (Fig. 4). After 1, 2, 4, 25 and 37 hours, 5-mL samples were withdrawn with glass volumetric pipettes, mixed with 5 mL of water in 20-mL scintillation vials and filtered as described earlier. Samples were refrigerated immediately after collection and retained for HPLC analysis. The cycle time on the Soxhlet extractors was about 15 minutes. Soil no. 2 was treated identically, except samples were withdrawn at 1, 2, 4, 24 and 48 hours.

8
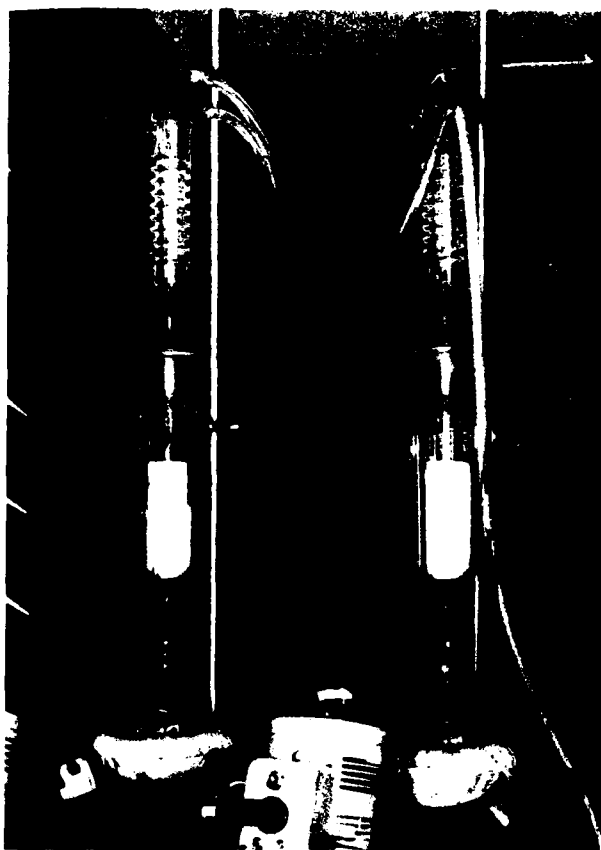
Figure 4. Soxhlet extractor.

## Analysis of variance experiment

Following the completion and assessment of the kinetic experiments, the four extraction procedures were compared. This was done by extracting six replicates of soil no. 6 by each approach using the amount of time appropriate for each method. For the wrist-action shaker and the Soxhlet extractor, we used 24-hour extraction periods. For the sonic bath and the soil-plant homogenizer, the periods were 4 hours and 10 minutes respectively. This experiment was conducted twice, once with acetonitrile and once with methanol, each containing a DNT internal standard. The extraction and analytical procedures used were identical to those described in the kinetic experiments. The soil was weighed out for these two experiments at one time in random order. All analyses for a given extraction solvent were conducted on a single day in duplicate, in random sequence. Mean values were compared using a two-way analysis of variance.

Subsequently, a similar study was conducted using all four methods and soil no. 2. The extraction times for each method were 24 hours for the Soxhlet, wrist-action shaker and bath sonifier, and 30 minutes for the soil-plant homogenizer.

9

# RESULTS AND DISCUSSION

## Soil no. 6

### Kinetic study

Our initial work was concentrated on soil no. 6 from the Iowa AAP. This soil was collected from an ordnance-burning area and was chosen because preliminary analysis indicated that it contained rather high levels of TNT and measurable amounts of HMX, RDX and TNB (a TNT degradation product). Initially, kinetic studies were conducted on each extraction method in an attempt to determine the length of time required to achieve equilibrium in the case of the three batch methods, or complete extraction in the case of the Soxhlet procedure. These results are presented in Appendix A, Table A1 for the soil-plant homogenizer, sonic bath, wrist-action shaker and Soxhlet extractor respectively. These data are plotted versus time in Figure 5. Example chromatograms for acetonitrile and methanol extracts are presented in Figure 6 for aliquots from the Soxhlet extractor versus time.

For the soil-plant homogenizer (Fig. 5a), short periods (1-16 minutes) were studied since this device grinds one sample at a time. Thus, from a practical point of view, it must reach equilibrium quickly or it is of no value, since in most USATHAMA applications a large number of samples will need to be analyzed. For the acetonitrile extracts, maximum values appear to be reached at 8 minutes for all four analytes. For methanol, there was a much slower rise and the solution was apparently not at equilibrium with the soil after 16 minutes. Care should be used when comparing the maximum values achieved in the two solvents since it is very difficult to obtain totally homogeneous subsamples of soil, and the differences in maximum values may be attributable to subsample inhomogeneity.

Since the ultrasonic bath method can process a large number of samples at a time, the use of fairly long time periods is practical. For that reason, we investigated times up to 4 hours (240 minutes)(Fig. 5b). For all four analytes, the highest values reached in both solvents were for the 4-hour samples. Since no longer periods were studied, there is no guarantee that maximum values have been obtained, although one reputed advantage of the ultrasonic bath method is its speed in reaching equilibrium. Again it is risky to compare the maximum values obtained for the two solvents on different subsamples; however, values for HMX in acetonitrile were nearly

10
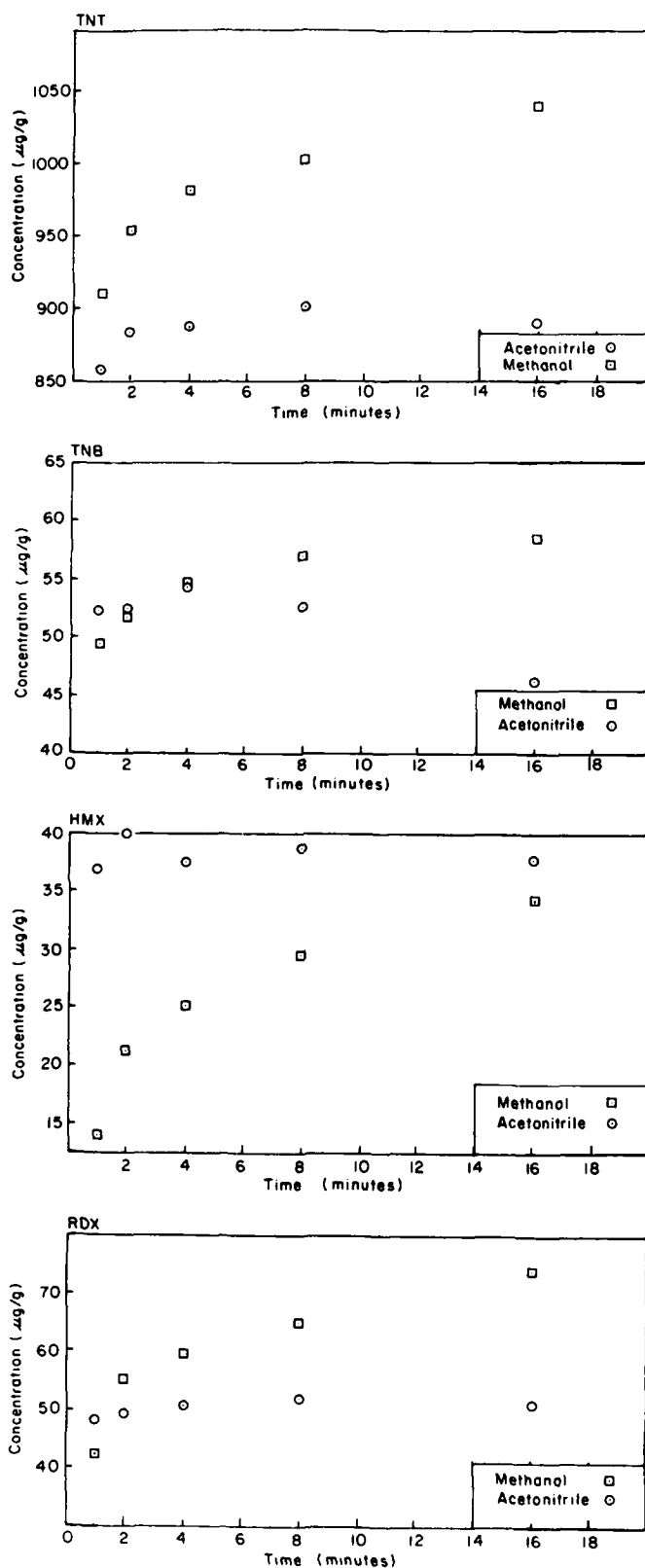
a.  Soil-plant homogenizer.

Figure 5.  Plots of analyte concentrations
for the kinetic study of Iowa AAP soil no. 6.

11
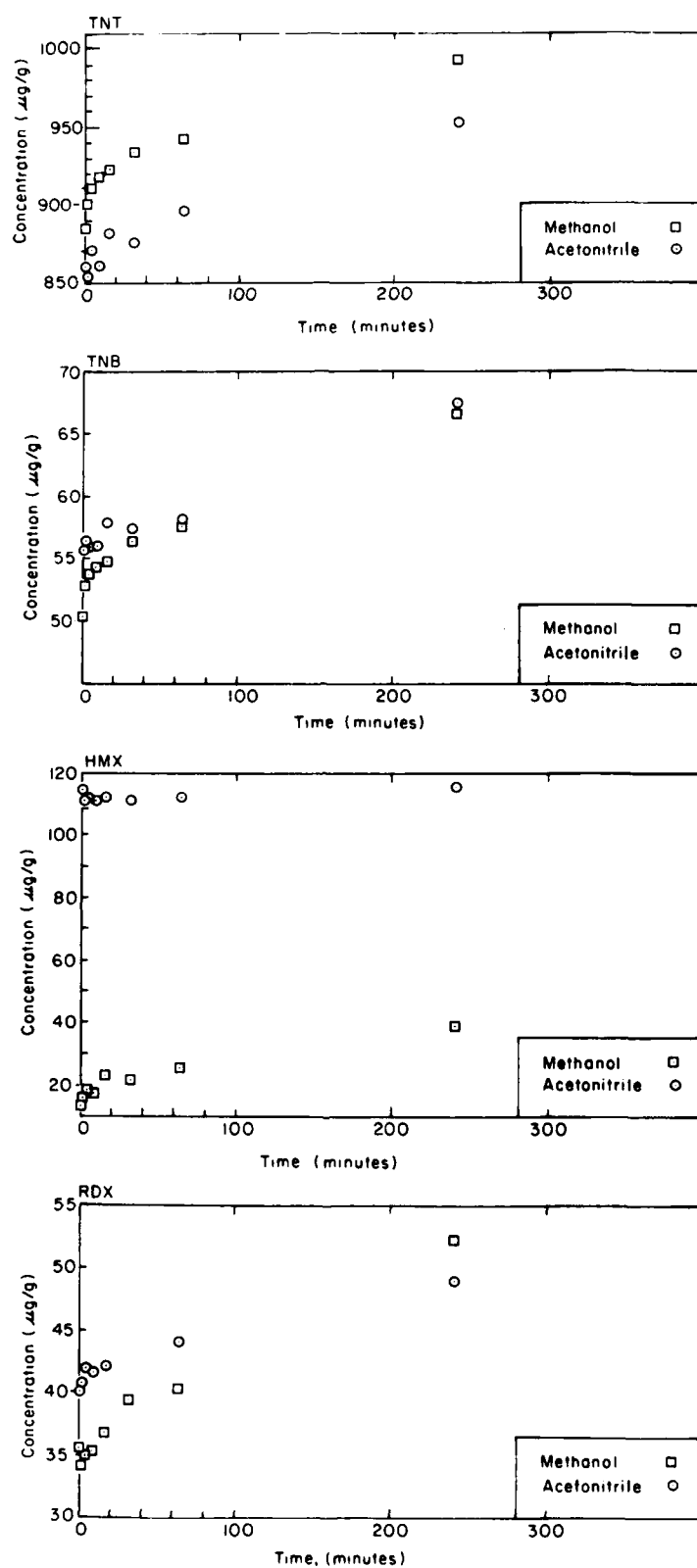
b. Sonic bath.

Figure 5 (cont'd). Plots of analyte concentrations for the kinetic study of Iowa AAP soil no. 6.

12
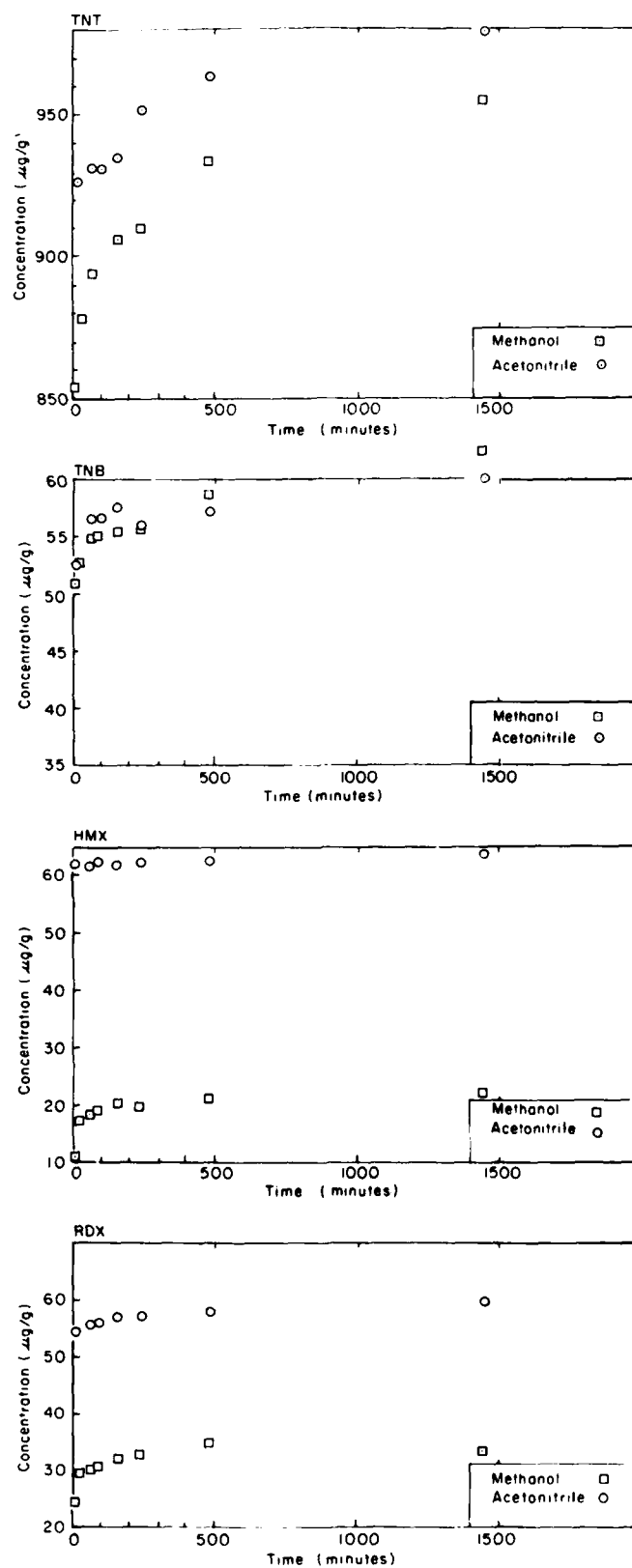
c. Wrist-action shaker.

Figure 5 (cont'd).

13
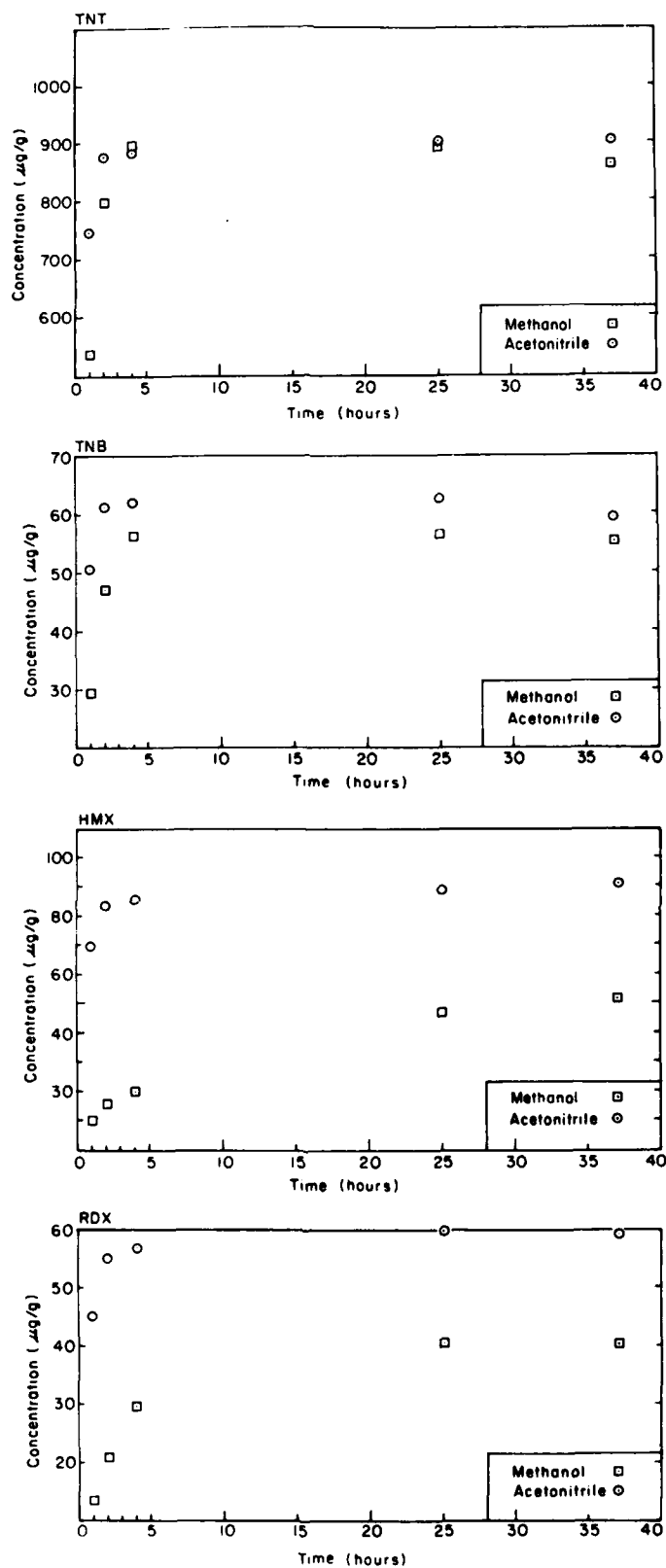
d. Soxhlet.

Figure 5 (cont'd). Plots of analyte concentrations for the kinetic study of Iowa AAP soil no. 6.

a. Methanol.  b. Acetonitrile.
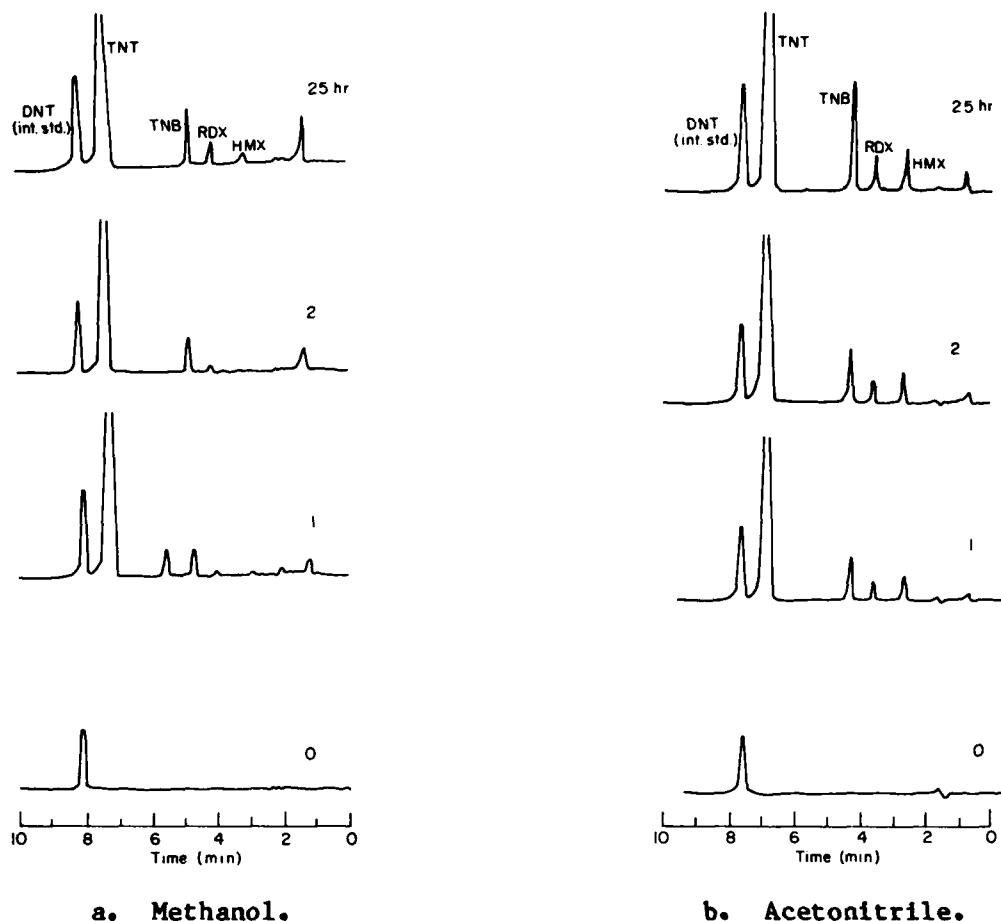
Figure 6. Example of chromatogram obtained for the kinetic study of Iowa
AAP soil no. 6 with the Soxhlet extractor.

three times those found for the methanol extract. The rate at which maximum values were achieved for HMX was also greater for acetonitrile.

The values obtained for the wrist-action shaker are shown in Figure 5c. Since up to 12 samples can be shaken simultaneously on the Burrell shaker with no one in attendance, use of long equilibrium periods is practical, if necessary. We tested times up to 24 hours (1440 minutes). For RDX and HMX, it appears that fairly constant values were obtained at 4 hours. For TNT and TNB, the highest values for both solvents were clearly found at 24 hours. Because of the scale of the figure, the 24-hour values for TNT appear to be much higher than the 4-hour values; however, the increase amounts to less than 2%. For TNB the increase amounts to only about 5%.

As was observed for the sonic bath, the values obtained for HMX were much lower in the methanol extract than in acetonitrile. RDX values were

also markedly less in the methanol extract, but this trend was not observed for either TNB or TNT.

Figure 5d presents the values found for the kinetic study with the Soxhlet extractor. This device differs from the other three in that the analytes are removed from interaction with the solid soil as they are extracted, rather than relying on a favorable equilibrium condition. In addition, the extracting solvent is heated well above room temperature and the extracted components are maintained at this elevated temperature for long periods. Thus the method does not depend on a favorable equilibrium, and complete separation of the analyte from the soil is possible. For TNT, TNB and RDX, maximum values seemed to be reached at 25 hours. For HMX, slightly higher values were obtained at 37 hours, but this increase only amounted to about 2% for acetonitrile and 8% for methanol. As previously observed, maximum values for HMX were much higher in the acetonitrile extracts than in methanol. RDX followed a similar pattern, while TNT and TNB were about the same in both solvents. The maximum values obtained by the Soxhlet method are in about the same range as those found by the other methods, indicating that solvent-soil partitioning is strongly in favor of solution.

The Soxhlet method was included in the study as a means of comparing the other methods. The Soxhlet requires a separate, relatively expensive setup for each sample and would be very expensive to use for analyzing large numbers of samples.

### Replicate study

To allow comparison of the four techniques, six replicate subsamples of soil no. 6 were processed by each method. The subsamples were weighed randomly and analyzed to allow comparisons of means and variances by standard analysis of variance techniques. The equilibrium times used were 10 minutes for the soil-plant homogenizer, 4 hours for the sonic bath and 24 hours for the wrist-action shaker. Soxhlet samples were also processed for 24 hours.

The individual values obtained for each method are presented in Table A2. The means and standard deviations for each analyte by each method are presented in Table 1 for acetonitrile and methanol.

Looking at the relative standard deviation (RSD), for both acetonitrile and methanol, it is clear that the analytes fall into two groups.

16

Table 1.  Means and standard deviations for replicate study
on Iowa AAP soil no. 6.

| Analyte | Method | Mean* (µg/g) | | Standard deviation (µg/g) | RSD (%) |
|---------|--------|-------------|---|----------------------------|---------|
| | | Acetonitrile Extract | | | |
| TNT | Shaker | 880.7 | a | 12.7 | 1.44 |
| | Sonic bath | 882.9 | a | 9.7 | 1.09 |
| | Homogenizer | 848.9 | b | 13.0 | 1.53 |
| | Soxhlet | 881.2 | a | 7.5 | 0.86 |
| TNB | Shaker | 55.1 | b | 1.0 | 1.88 |
| | Sonic bath | 55.6 | b | 0.6 | 1.04 |
| | Homogenizer | 51.4 | c | 0.8 | 1.51 |
| | Soxhlet | 62.1 | a | 1.1 | 1.83 |
| RDX | Shaker | 54.2 | a | 9.7 | 17.9 |
| | Sonic bath | 54.5 | a | 13.3 | 24.3 |
| | Homogenizer | 64.4 | a | 55.8 | 86.7 |
| | Soxhlet | 65.1 | a | 10.6 | 16.3 |
| HMX | Shaker | 82.0 | a | 31.9 | 38.9 |
| | Sonic bath | 56.4 | a | 14.4 | 25.5 |
| | Homogenizer | 64.9 | a | 26.8 | 41.2 |
| | Soxhlet | 84.1 | a | 11.5 | 13.6 |
| | | Methanol Extract | | | |
| TNT | Shaker | 895.4 | a | 14.3 | 1.60 |
| | Sonic bath | 840.4 | b | 25.0 | 2.97 |
| | Homogenizer | 870.2 | a | 38.7 | 4.44 |
| | Soxhlet | 891.4 | a | 5.1 | 0.57 |
| TNB | Shaker | 56.0 | b | 0.8 | 1.37 |
| | Sonic bath | 52.5 | c | 1.5 | 2.90 |
| | Homogenizer | 53.4 | c | 1.1 | 1.97 |
| | Soxhlet | 58.3 | a | 0.6 | 1.08 |
| RDX | Shaker | 36.9 | a | 11.8 | 31.9 |
| | Sonic bath | 39.9 | a | 7.8 | 19.6 |
| | Homogenizer | 30.9 | a | 16.6 | 53.7 |
| | Soxhlet | 48.0 | a | 5.3 | 10.9 |
| HMX | Shaker | 22.3 | a | 5.4 | 24.2 |
| | Sonic bath | 33.4 | a | 10.6 | 31.6 |
| | Homogenizer | 28.4 | a | 18.0 | 63.5 |
| | Soxhlet | 58.8 | a | 5.8 | 9.8 |

*Values indicated with the same letter are not significantly
different at the 95% confidence level.

The RSD for TNT and TNB is generally in the range of 1-3%, indicating very good analytical precision, as well as good soil homogenization prior to subsampling. The RSD for RDX and HMX, on the other hand, is quite large, generally at or above 20% and for the homogenizer sometimes over 50%. The mean values for HMX and RDX are about the same as that for TNB, and hence this difference in RSD is apparently not a result of differences in the mean concentration. It thus appears that RDX and HMX are distributed differently, and less homogeneously, than TNT and TNB in this soil. Because of the much larger sample size for the Soxhlet procedure (16 g vs either 1 or 2 g), RSD values for the Soxhlet procedure are lower than those for the other methods for HMX and RDX in both solvents. In addition, RSD values for the homogenizer, where 1-g subsamples were used, were generally higher than for the shaker and sonic bath where 2-g subsamples were used, as we expected (Grant and Pelton 1976).

Because of the very good precision and low random error obtained for TNT, analysis of variance (Table 2) indicates a significant difference for the methods at the 95% confidence level. For TNT, the Soxhlet and wrist-action shaker give very similar results with both solvents. The soil-plant homogenizer gives significantly lower values with acetonitrile while the sonic bath is low for methanol. This results in a significant interaction between method and solvent at the 95% confidence level, even though the difference between solvents is not significant overall.

For TNB, excellent precision also enables sensitive comparison of the various extraction procedures and solvents (Table 1); method, solvent and interaction are all significant at the 95% confidence level (Table 2). With both solvents, the Soxhlet procedure is clearly superior to the other three methods with respect to the amount extracted, the largest difference being observed with acetonitrile. The reason for this superiority of the Soxhlet for TNB but not for TNT is unclear, particularly because of the similarity in structure for the two substances. As was observed for TNT, extraction using the sonic bath is clearly better with acetonitrile than methanol while the opposite is true for the soil-plant homogenizer.

The sensitivity of the analysis of variance for RDX and HMX is limited by the large standard deviations for both analytes. This large random error makes it impossible to observe the small differences in the various methods observed for TNT and TNB. Thus in neither case was method found to be significant at the 95% confidence level.

18

Table 2. Results of two-way analysis of variance for Iowa
AAP soil no. 6.

|  | SS | df | Mean square | F |
|---|---|---|---|---|
| **TNT** | | | | |
| Method | 8511.22 | 3 | 2837.07 | 8.02* |
| Solvent | 11.02 | 1 | 11.02 | 0.03 |
| Interaction | 7732.83 | 3 | 2577.61 | 7.29* |
| Error | 14146.9 | 40 | 353.67 | |
| LSD = 29.2 | | | | |
| **TNB** | | | | |
| Method | 404.13 | 3 | 134.7 | 139.11* |
| Solvent | 11.43 | 1 | 11.43 | 11.8* |
| Interaction | 75.58 | 3 | 25.19 | 26.02* |
| Error | 38.73 | 40 | 0.9683 | |
| LSD = 1.53 | | | | |
| **RDX** | | | | |
| Method | 846.13 | 3 | 282.04 | 0.59 |
| Solvent | 4503.3 | 1 | 4503.3 | 9.39* |
| Interaction | 348.2 | 3 | 116.0 | 0.24 |
| Error | 19177.9 | 40 | 479.45 | |
| **HMX** | | | | |
| Method | 5329.2 | 3 | 1776.4 | 5.53 |
| Solvent | 15668.2 | 1 | 15668.5 | 48.77* |
| Interaction | 2539.2 | 3 | 846.4 | 2.63 |
| Error | 12850.2 | 40 | 321.3 | |

* Values are significant at the 95% confidence level.
Critical values are $F(3,40) = 2.84$ and $F(1,40) = 4.08$.

Solvent, on the other hand, was found to be significant for TNB, RDX
and HMX even with the large random error variance of the latter two explo-
sives. Use of acetonitrile clearly resulted in higher extraction effi-
ciency for both substances. Whether this is a thermodynamic difference
attributable to solubility, or to an unfavorable partition coefficient or a
kinetic one, is unclear. The solubilities of RDX and HMX are higher in
acetonitrile than in methanol (unpublished data, D.C. Leggett); therefore
partitioning is also expected to be more favorable into acetonitrile. In

19

either case, from a practical point of view, acetonitrile is clearly superior for RDX and HMX extraction with this soil.

## Soil no. 2

### Kinetic Study

Following the work with soil no. 6, it was of interest to us to determine if similar behavior would be observed with a different soil, particularly one with much lower TNT concentrations. Preliminary analysis indicated that the Iowa AAP soil no. 2 had much lower, but measurable, concentrations of TNT and traces of TNB, RDX and HMX. This soil was from an old disposal lagoon and hence the mode of contamination should have been somewhat different from that of soil no. 6, which came from an ordnance burning area.

A kinetic study similar to that conducted with soil no. 6 was done first. All four extraction methods were tested with both acetonitrile and methanol. Because of the results with soil no. 6, equilibration times were modified from those used earlier. In particular, the longest time increments for the Soxhlet and wrist-action shaker were extended to 48 hours. The results of this kinetic study are presented in Table A3 and plotted in Figure 7 for TNT. Only trace levels were obtained for TNB, RDX and HMX, and since the peaks were not consistently integrated, no attempt was made to quantify these substances. Examples of chromatograms obtained for extracts from the wrist-action shaker are presented in Figure 8.

TNT levels were indeed much lower for soil no. 2 than for soil no. 6. The kinetics of desorption was also slower for all four methods. Thus, it is likely that TNT in soil no. 2 was associated with the soil in a somewhat different manner than it was in soil no. 6. Since soil no. 2 is from the surface of a disposal lagoon, it is likely that TNT associated with this soil was initially present in solution and became associated through adsorption as water evaporated from the surface or percolated through. Soil no. 6 was from an ordnance burning area, and it is likely that TNT became associated with this soil as discrete crystals, which may have dissolved and reassociated through rainfall and transpiration.

One explanation that may account for the slower desorption kinetics observed for soil no. 2 is that the low level of TNT present in this soil is preferentially adsorbed to high energy binding sites. Since the number of these types of sites is limited, the large amount of TNT associated with soil no. 6 probably exceeds what can be adsorbed in this fashion. The bulk

20
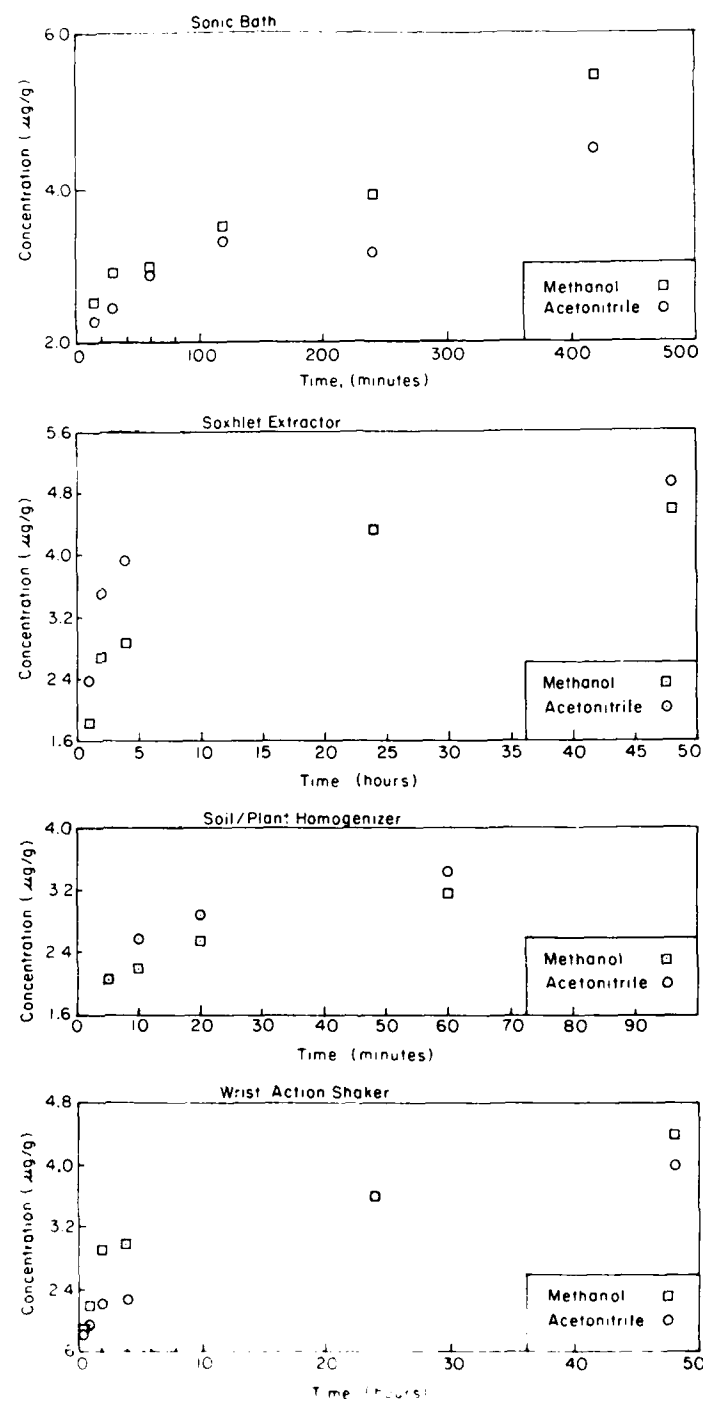
Figure 7. Plots of TNT values for the kinetic study of Iowa AAP soil no. 2.

21

a.  Acetonitrile.                    b.  Methanol.
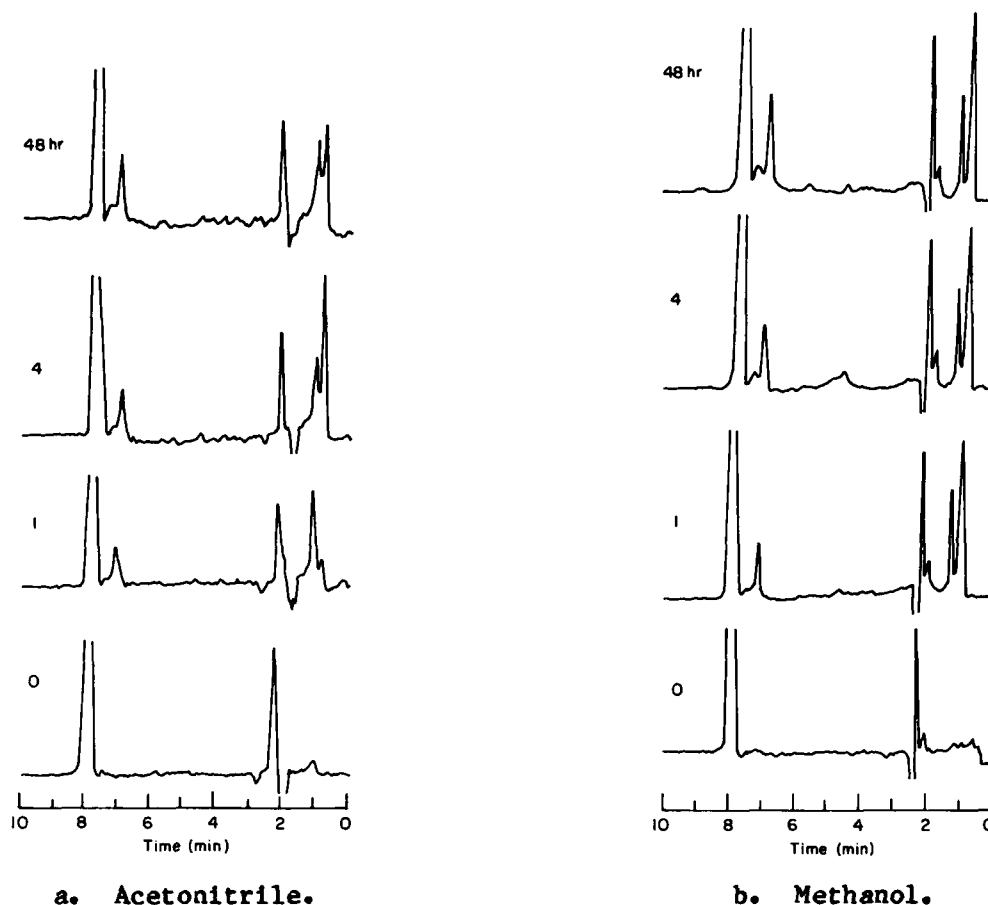
Figure 8.   Example of chromatogram obtained for the kinetic study
of Iowa AAP soil no. 2 with the wrist-action shaker.

of the TNT may therefore be less tightly bound.  The activation energy for
desorption of this material would be lower, resulting in faster desorption
kinetics.

Looking at the kinetic results (Fig. 7), it appears that in none of
the four methods was equilibrium definitely established during the experi-
ment for either solvent.  The Soxhlet and wrist-action shaker appear to be
closer to a terminal value for the times studied than do the soil-plant
homogenizer or the sonic bath, which were both studied for shorter per-
iods.  Little difference was observed between solvents.  Clearly, use of
the soil-plant homogenizer for extended periods is impractical since it is
a one-sample-at-a-time technique and, in addition, results in a large
degree of solvent evaporation since the tubes are required to be open to
the atmosphere during grinding.  Use of the sonic bath for longer periods
is possible, however.  The wrist-action shaker and Soxhlet appear to have

22

come fairly close to final values after 24 hours and, from a practical
point of view, this is about the maximum time acceptable for soil equili-
bration-extraction. Thus for the next phase, the replicate study, we
decided to compare the four techniques using a 24-hour period for the
Soxhlet, the wrist-action shaker and the sonic bath and 30 minutes for the
soil-plant homogenizer.

### Replicate study

As with soil no. 6, six replicate subsamples of soil no. 2 were
extracted by each of the same four techniques. Methanol and acetonitrile
were both tested at the time periods described above. The individual
results for TNT and TNB are presented in Table A4. Mean values and
standard deviations are presented in Table 3 and the results of a two-way
analysis of variance in Table 4.

Table 3. Means and standard deviations for replicate study
on Iowa AAP soil no. 2.

| Mean | Mean (µg/g) | Standard deviation (µg/g) | RSD (%) | Extract |
|------|------|------|------|------|
| | | TNT | | |
| Shaker | 2.46 c | 0.124 | 5.04 | Acetonitrile |
| Sonic bath | 3.54 b | 0.223 | 6.30 | |
| Homogenizer | 2.10 d | 0.108 | 5.14 | |
| Soxhlet | 4.35 a | 0.327 | 7.51 | |
| Shaker | 2.76 b | 0.252 | 9.12 | Methanol |
| Sonic bath | 3.91 a | 0.194 | 4.97 | |
| Homogenizer | 2.23 c | 0.079 | 3.55 | |
| Soxhlet | 3.68 a | 0.106 | 2.89 | |
| | | TNB | | |
| Shaker | 0.366 a | 0.047 | 12.8 | Acetonitrile |
| Sonic bath | 0.449 a | 0.105 | 23.4 | |
| Homogenizer | 0.348 a | 0.127 | 36.5 | |
| Soxhlet | 0.332 a | 0.051 | 15.4 | |
| Shaker | 0.311 a,b | 0.087 | 28.0 | Methanol |
| Sonic bath | 0.444 a | 0.118 | 26.6 | |
| Homogenizer | 0.265 b | 0.078 | 29.4 | |
| Soxhlet | 0.273 b | 0.059 | 21.6 | |

*Values indicated with the same letter are not significantly
different at the 95% confidence level.

23

Table 4. Results of two-way analysis of variance
for Iowa AAP soil no. 2.

|  | SS | df | Mean square | F |
|---|---|---|---|---|
|  |  | **TNT** |  |  |
| Method | 27.93 | 3 | 9.31 | 244.8* |
| Solvent | 0.0096 | 1 | 0.0096 | 0.5 |
| Interaction | 2.029 | 3 | 0.6764 | 17.78* |
| Error | 1.521 | 40 | 0.0380 |  |

LSD = 0.302

|  | SS | df | Mean square | F |
|---|---|---|---|---|
|  |  | **TNB** |  |  |
| Method | 0.1635 | 3 | 0.0545 | 6.96* |
| Solvent | 0.0305 | 1 | 0.0306 | 3.90 |
| Interaction | 0.0095 | 3 | 0.0032 | 0.40 |
| Error | 0.3132 | 40 | 0.0078 |  |

LSD = 0.137

*Values are significant at the 95% confidence level.
Critical values are F(3,40) = 2.84 and F(1,40) = 4.08.

Experimental precision for TNT averaged about 6% (RSD), indicating very good soil homogenization prior to subsampling. This excellent precision allowed a powerful comparison among methods using analysis of variance techniques, which indicated a significant difference among methods but no consistent difference between solvents. For acetonitrile, the Soxhlet was significantly better than the other three procedures; the sonic bath was second. For methanol, the sonic bath and the Soxhlet were not significantly different but were significantly higher than the shaker or homogenizer. There was a significant interaction between method and solvent, indicating that some methods worked better in one solvent while another method worked better in the other one.

For TNB, the relative standard deviation was somewhat larger than for TNT, averaging over 20%. This is a result of the very low levels of TNB present in this soil (about 0.4 µg/g), which approached the detection limit, estimated at about 0.1 µg/g. RSD values typically increase as levels approach the detection limit.

Analysis of variance for the TNB results indicated a significant difference existed among methods but not for solvent type or method-solvent interaction. This significant difference in methods was only apparent in methanol, where the sonic bath resulted in significantly higher results than the Soxhlet or homogenizer. The shaker was not significantly different from any of the other three methods at the 95% confidence level.

In addition to lower recovery for the Soxhlet procedure for TNB, it had a second disadvantage. This was the much higher extraction of other substances that tended to interfere with HPLC analysis. The major interferant appeared to be the aminodinitrotoluenes, which elute between TNT and DNT (the internal standard).

## CONCLUSIONS AND RECOMMENDATIONS

The results of this study are complicated and no simple explanation adequately describes all of the findings. Clearly methanol and acetonitrile were equally good for extraction of TNT. For RDX and HMX, acetonitrile was superior both kinetically and thermodynamically. For TNB, acetonitrile appears to be better only at higher concentrations. Overall it appears that acetonitrile is the solvent of choice.

Of the four methods tested, the ultrasonic bath and Soxhlet typically result in higher analyte recovery. For the low-level soil (soil no. 2), samples were equilibrated in the ultrasonic bath for 24 hours and generally it resulted in analyte concentrations equivalent to the Soxhlet and better than the homogenizer or shaker. For the high level sample (soil no. 6), the ultrasonic bath was tested with only a 4-hour equilibration period. Even so, the recovery with acetonitrile was excellent for TNT and only slightly less than the Soxhlet for TNB. It probably would have proved equivalent to Soxhlet overall if a 24-hour equilibration had been used.

The sonic bath is also a practical choice since it can be used to process a number of samples simultaneously. It can also be used in an unattended fashion and is relatively inexpensive. Typically, these devices run about $800. The gentle heating that occurs with the sonic bath (≈ 38°C) also seems desirable to increase the rate at which equilibrium is attained. The sonic bath does not suffer from the problem experienced with the Soxhlet device of co-extracting significant amounts of interfering substances that have a low solvent-soil partition coefficient.

The wrist-action shaker is desirable because of its simplicity, ability to process a large number of samples in an unattended manner, and low cost. While it appeared to work rather well for TNT for the high concentration soil, it provided very poor recovery for TNT in the low level sample. For TNB it was generally equivalent to the sonic bath.

The plant-soil homogenizer suffers from the restriction of processing one sample at a time. This limits its practical equilibration time as does significant solvent evaporation. Equilibrium is not established quickly enough and the homogenizer extracts were generally much lower in concentration than any of the other procedures. Because of these findings we do not feel this device deserves further consideration.

The Soxhlet extractor has long been the accepted method for extracting trace organics from soil matrices. It generally resulted in excellent recovery of TNT and TNB compared to the other techniques in this study. However, it requires a separate, fairly expensive setup for each sample and as mentioned earlier would be very expensive to use if large numbers of sample analyses were needed. For organics with very poor solvent-soil partition coefficients, the Soxhlet is particularly desirable. Explosive residues generally have very favorable partition coefficients and hence this advantage is not particularly useful. The disadvantage of extracting interferences with low partition coefficients was observed here.

Overall, we feel that the ultrasonic bath has the greatest potential for use in extracting explosive residues from soil and possibly sediment. Additional work with more soils, and with sediments, concentrating on the kinetics of extraction, would be useful before a final recommendation is possible. It would be very desirable to understand the relationship between the rate and extent of analyte extraction and its mode of adsorption-interaction with the soil.

LITERATURE CITED

Cragin, J.H., D.C. Leggett, B.T. Foley and P.W. Schumacher (1985) TNT, RDX, and HMX in soils and sediments. Analysis techniques and drying losses. USA Cold Regions Research and Engineering Laboratory, CRREL Report 85-15 (THAMA Report AMX-TH-TE-TR-85038).

Dao, T.H., T.L. Lavy and J. Dragun (1983) Rationale of solvent selection for soil extraction of pesticide residues. In Residue Reviews, vol. 87 (F.A. Gunther and J.D. Gunther, Ed.). New York: Springer-Verlag, pp. 91-104.

Freeman, D.H. and L.S. Cheung (1981) A gel partition model for organic desorption from a pond sediment. Science, 214:790-792.

Goerlitz, D.F. and L.M. Law (1975) Gas chromatographic method for the analysis of TNT and RDX explosives contaminating water and soil-core material. U.S. Geological Survey, Open File Report 75-182.

Grant, C.L. and P.A. Pelton (1976) Influence of sampling on the quality of analyses with emphasis on powders. Advances in X-Ray Analysis, vol. 17 (C.L. Grant, Ed.). New York: Plenum Press.

Haddock, J.D., P.F. Landrun and J.P. Glesy (1983) Extraction efficiency of anthracene from sediments. Analytical Chemistry, 55(7): 1197-1200.

Jenkins, T.F., C.F. Bauer, D.C. Leggett and C.L. Grant (1984) Reverse phase HPLC method for analysis of TNT, RDX, HMX and 2,4-DNT in munitions wastewater. USA Cold Regions Research and Engineering Laboratory, CRREL Report 84-29.

Miller, H.H., M.V. Cook and J.L. Spigarelli (1983) Development of sampling and preservation techniques to retard chemical and biological changes in water samples. Final Report, Contract No. DAAK11-81-C-007. Kansas City, Missouri: Midwest Research Institute.

Peterson, J.C. and D.H. Freeman (1982) Method validation of GC-MS-SIM analysis of phthalate esters in sediment. International Journal of Environmental Analytical Chemistry, 12: 277-291.

Sporstol, S., N. Gjos and G.E. Carlberg (1983) Extraction efficiencies for organic compounds found in aquatic sediments. Analytica Chimica Acta, 151: 231-235.

Wegman, R.C.C. and A.W.M. Hofster (1982) Determination of organochlorine in river sediment by capillary gas chromatography. Water Research, 16: 1265-1272.

# APPENDIX A:  EXPERIMENTAL DATA

## Table A1.  Kinetic study of Iowa AAP Soil no. 6 ($\mu g/g$).

| Time (min) | HMX | RDX | TNB | TNT | Extract |
|---|---|---|---|---|---|
| | | Soil-Plant homogenizer | | | |
| 1 | 36.8 | 48.2 | 52.2 | 857 | Acetonitrile |
| 2 | 39.9 | 49.4 | 52.3 | 883 | |
| 4 | 37.4 | 51.0 | 54.3 | 887 | |
| 16 | 37.7 | 51.3 | 46.3 | 891 | |
| | | | | | |
| 1 | 14.1 | 42.3 | 49.4 | 910 | Methanol |
| 2 | 21.1 | 55.3 | 51.7 | 953 | |
| 4 | 25.1 | 59.8 | 34.1 | 981 | |
| 8 | 29.4 | 65.2 | 56.9 | 1002 | |
| 16 | 34.0 | 74.1 | 58.6 | 1041 | |
| | | Sonic Bath | | | |
| 1 | 114 | 40.1 | 55.8 | 860 | Acetonitrile |
| 2 | 111 | 40.8 | 56.8 | 854 | |
| 4 | 112 | 41.9 | 56.8 | 871 | |
| 8 | 111 | 41.7 | 55.9 | 861 | |
| 16 | 112 | 42.2 | 57.9 | 882 | |
| 32 | 111 | 42.7 | 57.4 | 876 | |
| 64 | 112 | 44.1 | 58.2 | 896 | |
| 240 | 115 | 48.9 | 67.4 | 952 | |
| | | | | | |
| 1 | 13.9 | 35.6 | 50.3 | 885 | Methanol |
| 2 | 16.1 | 34.2 | 52.8 | 901 | |
| 4 | 18.0 | 35.0 | 53.6 | 912 | |
| 8 | 17.6 | 35.3 | 54.3 | 919 | |
| 16 | 23.2 | 36.9 | 54.9 | 923 | |
| 32 | 21.9 | 39.5 | 56.4 | 934 | |
| 64 | 25.7 | 40.4 | 57.6 | 943 | |
| 240 | 38.9 | 52.2 | 66.5 | 992 | |
| | | Wrist-action shaker | | | |
| 10 | 62.0 | 54.3 | 52.5 | 926 | Acetonitrile |
| 60 | 61.7 | 55.6 | 56.6 | 931 | |
| 90 | 62.5 | 56.0 | 56.7 | 931 | |
| 150 | 62.0 | 56.7 | 57.8 | 935 | |
| 240 | 62.3 | 57.0 | 56.0 | 952 | |
| 480 | 62.5 | 58.0 | 57.3 | 963 | |
| 1440 | 63.7 | 59.8 | 60.1 | 979 | |

29

Table A1 (cont'd.)

| Time (hr) | HMX | RDX | TNB | TNT | Extract |
|-----------|-----|-----|-----|-----|---------|
| 10 | 10.9 | 24.3 | 50.8 | 854 | Methanol |
| 30 | 17.1 | 29.6 | 53.0 | 878 | |
| 60 | 18.5 | 30.1 | 54.9 | 894 | |
| 90 | 18.8 | 30.7 | 55.1 | 894 | |
| 150 | 20.6 | 32.3 | 55.5 | 906 | |
| 240 | 19.8 | 32.8 | 56.0 | 910 | |
| 480 | 21.2 | 34.9 | 58.7 | 933 | |
| 1440 | 22.2 | 33.4 | 62.4 | 955 | |

Soxhlet

| Time (hr) | HMX | RDX | TNB | TNT | Extract |
|-----------|-----|-----|-----|-----|---------|
| 1 | 69.5 | 45.5 | 50.9 | 746 | Acetonitrile |
| 2 | 83.5 | 55.4 | 61.2 | 877 | |
| 4 | 85.7 | 57.1 | 62.0 | 882 | |
| 25 | 88.2 | 60.1 | 62.5 | 902 | |
| 37 | 90.0 | 59.2 | 59.1 | 903 | |
| 1 | 10.3 | 13.3 | 29.5 | 537 | Methanol |
| 2 | 16.1 | 20.9 | 47.3 | 799 | |
| 4 | 20.3 | 30.0 | 56.4 | 899 | |
| 25 | 47.0 | 40.8 | 56.4 | 890 | |
| 37 | 51.1 | 40.4 | 55.1 | 860 | |

Table A2. Replicate study of Iowa AAP soil no. 6 ($\mu$g/g).

| Wrist-action shaker | Sonic bath | Soil-plant homogenizer | Soxhlet extractor | Extract |
|---------------------|------------|------------------------|-------------------|---------|
| | | TNT | | |
| 900.7 | 882.2 | 868.5 | 890.7 | Acetonitrile |
| 884.1 | 880.8 | 846.4 | 874.4 | |
| 867.6 | 896.7 | 859.5 | 874.9 | |
| 872.0 | 891.6 | 832.6 | 876.8 | |
| 871.5 | 872.2 | 844.8 | 890.5 | |
| 888.4 | 873.9 | 841.3 | 879.6 | |
| 895.5 | 811.9 | 857.1 | 892.2 | Methanol |
| 882.7 | 828.8 | 863.0 | 893.7 | |
| 895.2 | 854.2 | 878.5 | 894.5 | |
| 913.9 | 815.1 | 849.4 | 896.9 | |
| 876.8 | 867.9 | 942.4 | 887.9 | |
| 908.5 | 864.7 | 831.0 | 882.9 | |

## Table A2 (Cont'd.)

| Wrist-action shaker | Sonic bath | Soil-plant homogenizer | Soxhlet extractor | Extract |
|---|---|---|---|---|
| | | TNB | | |
| 55.7 | 56.1 | 50.7 | 63.6 | Acetonitrile |
| 55.4 | 55.8 | 51.5 | 61.8 | |
| 53.8 | 55.3 | 52.1 | 61.6 | |
| 54.2 | 55.9 | 50.3 | 63.1 | |
| 54.7 | 55.7 | 51.2 | 62.0 | |
| 56.6 | 54.5 | 52.3 | 60.4 | |
| | | | | |
| 56.5 | 50.5 | 53.0 | 59.3 | Methanol |
| 55.4 | 52.4 | 52.0 | 58.6 | |
| 56.3 | 52.7 | 53.6 | 58.3 | |
| 57.0 | 51.1 | 53.9 | 57.8 | |
| 55.0 | 54.4 | 55.1 | 57.9 | |
| 55.5 | 53.9 | 52.9 | 57.6 | |
| | | RDX | | |
| 47.4 | 47.4 | 45.1 | 66.8 | Acetonitrile |
| 49.0 | 69.1 | 44.3 | 68.6 | |
| 58.6 | 48.4 | 37.5 | 83.0 | |
| 46.0 | 42.3 | 33.4 | 62.7 | |
| 52.5 | 46.1 | 177.8 | 53.1 | |
| 71.7 | 73.4 | 48.4 | 56.4 | |
| | | | | |
| 40.7 | 31.8 | 33.3 | 48.1 | Methanol |
| 30.1 | 38.6 | 31.3 | 57.2 | |
| 30.6 | 37.7 | 56.9 | 44.7 | |
| 33.5 | 54.9 | 34.7 | 48.2 | |
| 27.5 | 39.4 | 30.9 | 41.5 | |
| 59.1 | 36.8 | 28.4 | 48.3 | |
| | | HMX | | |
| 71.9 | 74.8 | 92.7 | 85.5 | Acetonitrile |
| 131.0 | 55.3 | 104.9 | 68.3 | |
| 88.8 | 73.2 | 50.4 | 72.5 | |
| 52.1 | 41.9 | 53.2 | 87.1 | |
| 101.6 | 46.5 | 44.6 | 96.2 | |
| 46.4 | 46.4 | 43.8 | 94.8 | |
| | | | | |
| 19.7 | 39.4 | 25.9 | 54.0 | Methanol |
| 21.4 | 39.4 | 19.3 | 67.6 | |
| 14.4 | 48.3 | 19.3 | 64.3 | |
| 22.8 | 28.0 | 27.1 | 57.2 | |
| 24.8 | 24.3 | 63.9 | 54.3 | |
| 30.6 | 21.1 | 14.6 | 55.3 | |

Table A3. Kinetic study of TNT extraction, Iowa AAP soil no. 2 ($\mu$g/g).

| Time (min) | Acetonitrile | Methanol |
|---|---|---|
| Soil-plant homogenizer | | |
| 5 | 2.05 | 2.03 |
| 10 | 2.57 | 2.12 |
| 20 | 2.87 | 2.53 |
| 60 | 3.42 | 3.16 |
| Sonic bath | | |
| 15 | 2.25 | 2.51 |
| 30 | 2.43 | 2.91 |
| 60 | 2.87 | 2.99 |
| 120 | 3.30 | 3.50 |
| 240 | 3.15 | 3.89 |
| 420 | 4.54 | 5.43 |
| Wrist-action shaker | | |
| 30 | 1.72 | 1.87 |
| 60 | 1.94 | 2.28 |
| 120 | 2.22 | 2.92 |
| 240 | 2.25 | 2.98 |
| 1440 | 3.62 | 3.60 |
| 2880 | 4.01 | 4.42 |
| Soxhlet | | |
| 1 | 2.39 | 1.82 |
| 2 | 3.49 | 2.68 |
| 4 | 3.93 | 2.86 |
| 24 | 4.31 | 4.31 |
| 48 | 4.85 | 4.55 |

Table A4. Replicate study of Iowa AAP soil no. 2 (µg/g).

| Wrist-action shaker | Sonic bath | Soil-plant homogenizer | Soxhlet | Extract |
|---|---|---|---|---|
| | | TNT | | |
| 2.50 | 3.75 | 2.07 | 3.76 | Acetonitrile |
| 2.44 | 3.29 | 2.07 | 4.36 | |
| 2.36 | 3.32 | 2.02 | 4.30 | |
| 2.47 | 3.69 | 2.03 | 4.39 | |
| 2.68 | 3.41 | 2.31 | 4.72 | |
| 2.33 | 3.77 | 2.11 | 4.55 | |
| | | | | |
| 2.86 | 3.80 | 2.15 | 3.66 | Methanol |
| 2.92 | 3.76 | 2.29 | 3.63 | |
| 2.44 | 3.78 | 2.21 | 3.69 | |
| 2.67 | 4.28 | 2.26 | 3.64 | |
| 2.54 | 3.92 | 2.33 | 3.88 | |
| 3.11 | 3.91 | 2.13 | 3.57 | |
| | | TNB | | |
| 0.417 | 0.331 | 0.321 | 0.380 | Acetonitrile |
| 0.285 | 0.556 | 0.294 | 0.263 | |
| 0.369 | 0.432 | 0.271 | 0.345 | |
| 0.401 | 0.596 | 0.343 | 0.322 | |
| 0.380 | 0.378 | 0.598 | 0.290 | |
| 0.342 | 0.403 | 0.260 | 0.392 | |
| | | | | |
| 0.231 | 0.330 | 0.238 | 0.270 | Methanol |
| 0.325 | 0.350 | 0.226 | 0.301 | |
| 0.244 | 0.379 | 0.410 | 0.337 | |
| 0.250 | 0.541 | 0.201 | 0.246 | |
| 0.456 | 0.628 | 0.294 | 0.312 | |
| 0.360 | 0.436 | 0.221 | 0.172 | |